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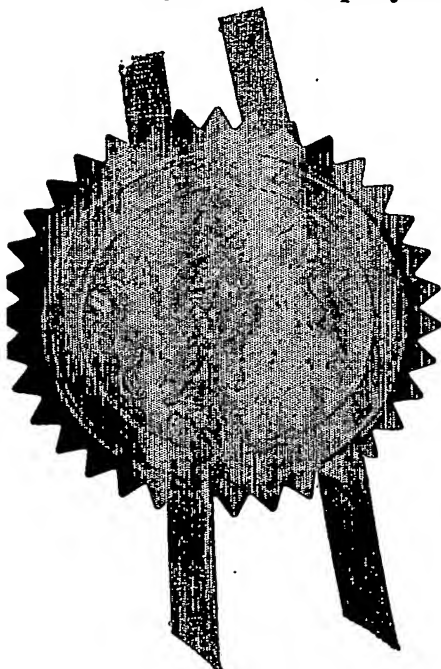
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GB0224267.5

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MIDDLESEX UNIVERSITY HIGHER EDUCATION CORPORATION

Incorporated in the United Kingdom

Bounds Green Road

London

N11 2NQ

United Kingdom

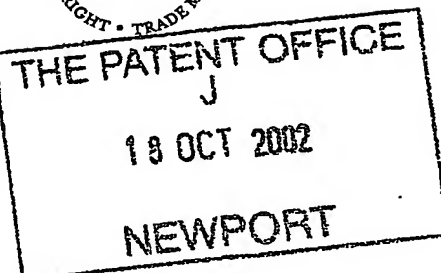
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P01/7700 00-024267.5

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2. Patent application number

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0224267.5

3. Full name, address and postcode of the or of each applicant (underline all surnames)

MIDDLESEX UNIVERSITY SERVICES LTD
BOUNDS GREEN ROAD
LONDON
N11 2NQ
GB

Patents ADP number (if you know it)

If the applicant is a corporate body, give country/state of its incorporation

SECTION 30 (1977 ACT) APPLICATION FILED 7.11.03

6822407001

4. Title of the invention

SENSORS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

COHEN, ALAN NICOL
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Patents ADP number (if you know it)

6963557001

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Country

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Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

1

6

3

1

2

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Priority documents

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

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I/We request the grant of a patent on the basis of this application.

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Date 17/10/82

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A. N. Cohen

01959 577172

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- 1 -

Sensors

The present invention relates to zirconia sensors; zirconia sensors are used for the detection of oxygen, carbon dioxide, water vapour etc.

5

Amperometric (two electrode) zirconia sensors are solid state electrochemical devices that have been developed and used principally for measuring oxygen in gas mixtures. Work has been reported where use has been extended to include measurement of water vapour or carbon dioxide. Adding a further pair of electrodes to the sensor enables it to be operated as a pump-gauge device which can still be used in the amperometric mode while providing additional information for analytical purposes via the gauge.

10

Amperometric zirconia sensors normally have a single enclosed internal volume and hence may be termed single-chamber devices. Some zirconia sensors have two enclosed internal volumes which may or not be connected to each other and to the external environment via a hole or holes and may be termed double-chamber devices; the inclusion of the second chamber confers additional benefits and this invention encompasses sensors with one, two or more chambers.

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Zirconia is an oxygen ion conductor at elevated temperatures ($>300^{\circ}\text{C}$) and its conductivity increases as the temperature is raised. Thus, by applying porous electronically-conducting electrodes, such as platinum, to the two surfaces of a disc of the ceramic, and imposing a voltage between the electrodes a current flows and oxygen is electrochemically pumped through the zirconia (amperometric mode); or, if the disc is in contact with gases having different oxygen partial pressures at each electrode then the system is a concentration cell and a Nernst EMF is generated between the two electrodes (potentiometric mode).

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One type of zirconia sensor comprises a hollow cylinder, one end of which comprises a disc of porous zirconia which disc has gas permeable electrodes on either side. The

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- 2 -

cylinder has a diffusion hole or holes formed within the structure connecting the inner volume of the hollow cylinder with the surrounding gas.

5 In use the sensor is heated and a potential difference applied across the disc via one pair of the electrodes; when a gas containing oxygen enters through the diffusion hole(s) the current flowing is a measure of the oxygen concentration in the gas surrounding the sensor.

10 Hitherto the sensor has been made by forming the sensor from a green (i.e. unfired) zirconia ceramic (formed from an intimate mixture of zirconia powder with a binder) e.g. by assembling discs and rings of the green zirconia ceramic to form the desired shape, inserting wires of e.g. platinum, to form electrical connections to the electrodes, printing, or painting or otherwise applying the electrodes onto the green zirconia ceramic, inserting and then removing a metal wire in the green zirconia
15 ceramic to form the diffusion hole and firing the structure.

The hole formed is adversely affected both by the pulling out of the wire and by the subsequent relaxation of the material surrounding the hole which can result in an imprecise and not well-defined hole. This affects the accuracy and repeatability of the
20 results from sensor to sensor.

We have now devised an improved method of forming the diffusion hole or holes which also enables holes with simple or complex geometries to be engineered.

25 According to the invention there is provided a method of forming a diffusion hole in a fired ceramic which method comprises forming a green ceramic structure from an intimate mixture of a powder of the ceramic and a binder which is normally a polymer, which structure incorporates an organic fibre or fibres or other organic element or elements passing from one side of the ceramic structure to the other in a
30 straight or non-straight path with uniform or non-uniform cross-section, firing the green ceramic structure at an elevated temperature to cure the ceramic and to destroy the binder and the organic fibre(s) or element(s).

- 3 -

For sensors, where the organic element is a fibre or fibres of uniform circular cross-section, the size diameter of the hole(s) after firing is preferably greater than 10 microns and more preferably in the range 25 to 200 microns and the size of the fibre(s) chosen accordingly. For zirconia ceramics there is a linear size reduction of about 20% on firing and this is allowed for in the dimensions of the green ceramic and fibre(s) or other organic elements.

The fibre can be destroyed by one or more of vapourisation, carbonisation, combustion or any other process which destroys the organic fibre.

The green ceramic can be formed by conventional methods such as by forming an intimate mixture of zirconia powder with a binder such as polyvinyl alcohol powder and a solvent such as water and forming into a sheet or tape. Discs and rings of this material are readily punched out from such a tape using simple steel tools.

The green structure can be fired in a conventional furnace to form a hard ceramic material and temperatures over 1000°C, e.g 1450°C, are typically used. At During the process of heating up to this temperature the organic fibre ~~will be~~ is vapourised or otherwise destroyed.

The sensor includes heating elements to raise the temperature of the sensor to the desired operating temperature e.g. of the order of 350-800°C. The heating element can be in the form of resistance wires in contact with, or embedded in or adjacent to the ceramic and an electric current can be fed to the heating element by means of platinum or other metal wires.

A preferred structure is for the heating element to be in the form of a circular or square disc, which may be made of alumina onto which is printed a metal film to carry the electrical current, in contact with, or adjacent to the zirconia ceramic structure; more preferably there can be two heating elements, one on either side of the sensor element to form a sandwich construction. The heating elements can be

connected in series or parallel; if they are in parallel there is still heating of if one heating element should fail.

5 A preferred method of making a sensor incorporating a sensor element, which may be a cylindrical sensor element or a planar sensor element or a sensor element of some other geometry, comprises placing the sensor element, plus heaters and thermal insulation where appropriate, on a support disc having a number of electrically isolated conductive wires/posts passing through and fixed to it, the wires/posts are positioned in a substantially circular configuration of diameter larger than the
10 diameter of the sensor element with the cylindrical or planar sensor element (including heaters and thermal insulation where appropriate) positioned within the circle formed by the wires/posts so that the wires/posts pass up the sides of the sensor element to grip the sensor element and connect to the contacts for the electrodes and for the heating elements. The wires/posts are normally then bent over at the ends to
15 grip and hold the sensor element.

In a further preferred embodiment the isolated conductive wires/posts pass through the support disc in a substantially circular configuration, they are bent at right angles outwards in a radial configuration, are then bent a second time at a point further
20 along the wires/posts so that the conductive wires/posts are again running essentially parallel to each other and perpendicular to the support disc but now in a substantially circular configuration which is of larger diameter than that at the point where the wires/posts traverse the support disc. The sensor, heater(s) and thermal insulation material are then introduced into the region between the wires/posts as above. In this
25 configuration there is a gap between the sensor element and the support disc.

In a further preferred embodiment the thermal insulation is cut as discs from sheet materials and is added in layers during assembly to fit within the circular arrangement of wires/posts. Alternatively, some or all of the discs of thermal insulation material
30 may be cut so as to extend beyond the diameter of the circular arrangement of

- 5 -

wires/posts; in this case either the wires/posts pass through the outer edges of such discs or the outer edges of some or all of the discs have a pattern cut in the circumference such that the wires/posts fit into the indentation generated. In each of these options each disc has a uniform thickness but thickness may vary from disc to disc

At the level where a heater and sensor are added a hole is normally cut in the accompanying layer or layers of insulation material so that the insulation material surrounds the active components and fills the gap between the heater or sensor and the wires/posts.

Each heater has two wires which are typically platinum connected to it to supply electrical power to the heating element. The sensor has at least two wires which are normally platinum running to it each wire connected to one of the sensor electrodes.

The wires from the heaters and from the sensor run between the layers of thermal insulation and are connected to the wires/posts running through the support disc. It is to be noted that with the method of packaging described, the sensor and heaters are not supported by the attaching wires and hence the diameters of the wires may be chosen on criteria other than mechanical strength, e.g. cost. A further benefit of this method of packaging is improved vibration and shock resistance of the sensor/heater(s).

The ends of the wires/posts on the other side of the disc from the sensor can be connected to an appropriate electricity supply e.g. for measuring the current flowing through the ceramic and for heating the element. If a standard BCB PCB (printed circuit board) socket is used this can be plugged into a standard board.

This structure is easy to fabricate and robust and easy to use.

The invention is illustrated in the drawings in which:-

Fig. 1 shows a cross section of a sensor element

Fig. 2 shows a cross section of an assembled sensor and

Figs. 3 and 4 show a preferred construction of a sensor

- 5 Referring to fig. 1 the sensor element is formed of a fired zirconia ceramic (1) which has an internal cavity (4), and a diffusion hole (3) formed in it by the method of the invention, there are platinum wires (2) which contact electrodes on the sensor as in conventional sensors. There is an electrical heating element (not shown) which heats up the sensor to operating temperature.

10

In use a potential difference is applied between wires (2) and, when a gas containing oxygen diffuses through the hole (3), the current flowing between the electrodes is a measure of the oxygen concentration.

- 15 Referring to fig. 2 the assembled sensor comprises a sensor element (9) as in fig. 1 on either side of which are heater elements (7) and (8).

- 20 Referring to Fig. 3 this shows the support for the assembled sensor and comprises a solid disc (10) into which wires (11) are fixed, the ends (11b) are arranged to plug into a socket such as a PCB socket which are commercially available. To assemble the sensor element the sensor, including heaters and thermal insulation material, is placed within the circle formed by the wires (fig. 4) and the wires (11) bent over the top of the sensor to grip and hold the sensor. All or some of the wires (11) are connected to the various components of the sensor so that the current flowing in the
- 25 sensor element can be measured and the heating elements operated.

Claims

1. A a method of forming a diffusion hole in a fired ceramic which method comprises forming a green ceramic structure from a powder of the ceramic which structure an
5 organic fibre or other organic element passing from one side of the ceramic structure to the other, firing the green ceramic structure at an elevated temperature to cure the ceramic and to destroy the organic fibre or other organic element.
2. A a method as claimed in claim 1 in which, where a fibre is employed, the size
10 diameter of the hole after firing is greater than 10 microns.
3. A a method as claimed in claim 1 in which, where a fibre is employed, the size diameter of the hole after firing is in the range 25 to 200 microns
4. A method as claimed in any one of claims 1 to 3 in which the green structure is
15 fired at a temperature in excess of 1000°C.
5. A method as claimed in any one of claims 1 to 4 in which the ceramic is zirconia.
6. A sensor which comprises a hollow cylinder with end caps enclosing an internal
20 volume having a hole or holes formed in its structure by the method of any one of claims 1 to 4, one end of the cylinder being a sensor element comprising a zirconia disc which has a porous electrode positioned on each surface, there being an electrical heating element able to heat the zirconia disc and in which sensor there are means
25 whereby a potential difference can be applied across the said disc between the electrodes and the current monitored.
7. A sensor which comprises a hollow cylinder with end and intermediate caps enclosing two or more internal volumes having one or more holes formed in its side
30 structure by the method of any one of claims 1 to 4, one end of the cylinder being a sensor element comprising a zirconia disc which has a porous electrode positioned on

each surface, there being an electrical heating element able to heat the zirconia disc and in which sensor there are means whereby a potential difference can be applied across the said disc between the electrodes and the current monitored or a constant current may be passed through the said disc or the electrodes on said disc are on open-circuit and a voltage is measured between said electrodes.

8. A sensor as claimed in claims 6 or 7 which comprises a sensor and an adjacent heating element which is close to or in contact with the sensor so that heating element is able to heat the sensor element.

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9. A sensor as claimed in claim 8 in which there are two heating elements one on each side of the sensor element to form a sandwich construction.

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10. A method of making a sensor incorporating a cylindrical or planar sensor element or a sensor element of some other geometry comprises placing the sensor element on a support disc having a number of electrically isolated conductive wires/posts passing through and fixed to it, the wires/posts are positioned in a substantially circular configuration of diameter larger than the diameter of the sensor element with the cylindrical sensor element positioned within the circle formed by the wires/posts so the wires/posts pass up the sides of the sensor element to grip the sensor element and connect to electrical contacts for the electrodes and for the heating elements.

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11. A method of making a sensor as in claim 10 in which the diameter of the circular configuration of wires/posts into which the sensor element is inserted is modified by bending each wire twice through a right angle prior to inserting the thermal insulation material and sensor element.

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12. A method of making a sensor as in claims 10 or 11 in which the thermal insulation material is added in layers of discs of a single thickness or varying thicknesses, each disc being cut from sheets of uniform thickness.

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- 9 -

13. A method of making a sensor as in claims 10 or 11 in which holes are cut in the discs of thermal insulation as appropriate to accommodate the sensor and heaters.
- 5 14. A method of making a sensor as in claims 12 and 13 in which the wires connecting the sensor and heaters to the wires/posts run between individual layers of discs of thermal insulation material.
- 10 15. A method of making a sensor as in claims 9 to 14 in which the wires/posts which pass up the sides of the sensor element are bent over at the end to grip the sensor element.
16. A sensor made by the methods of claims 9 to 15.
- 15 17. A sensor as hereinbefore described with reference to the drawings.

- 10 -

Abstract

- 5 In a zirconia oxygen sensor utilising a diffusion hole the hole is made by inserting an organic fibre or element in the green ceramic and firing to destroy the fibre or element and leave a hole in its place. A package for a sensor is described in which the wire/posts for the electrical connections also form a cage to hold the sensor, heater(s) and thermal insulation firmly and plug into an electrical socket.

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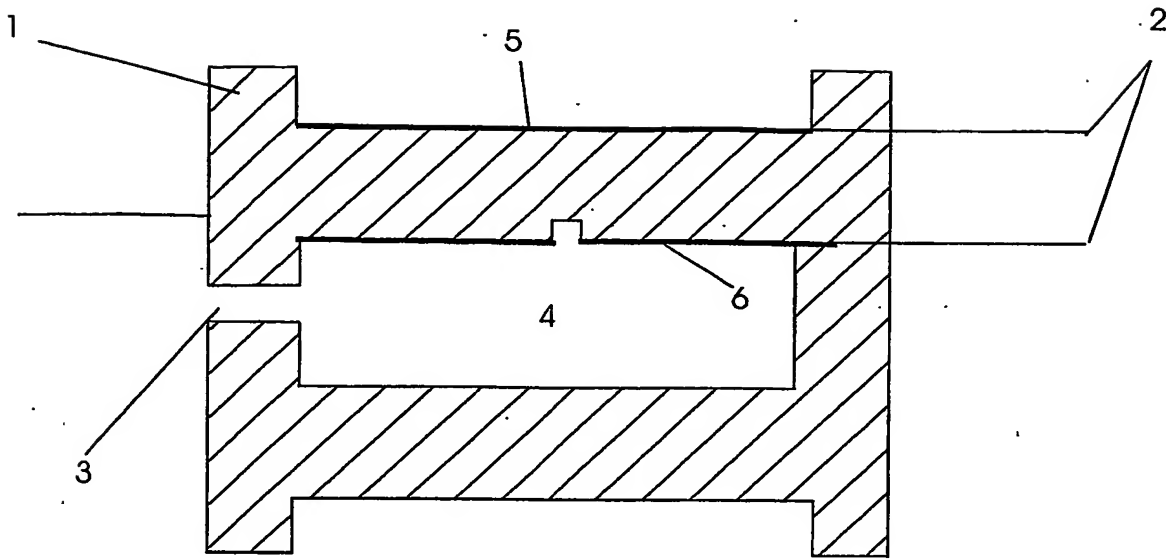


Fig. 1

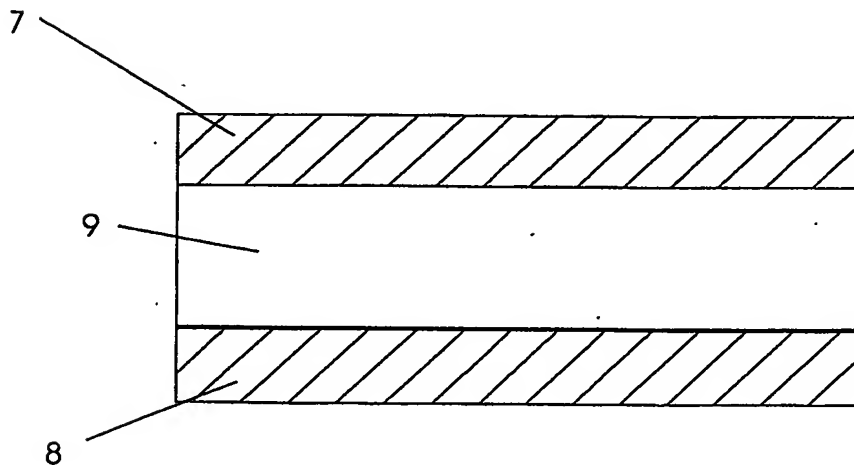


Fig. 2

2/2

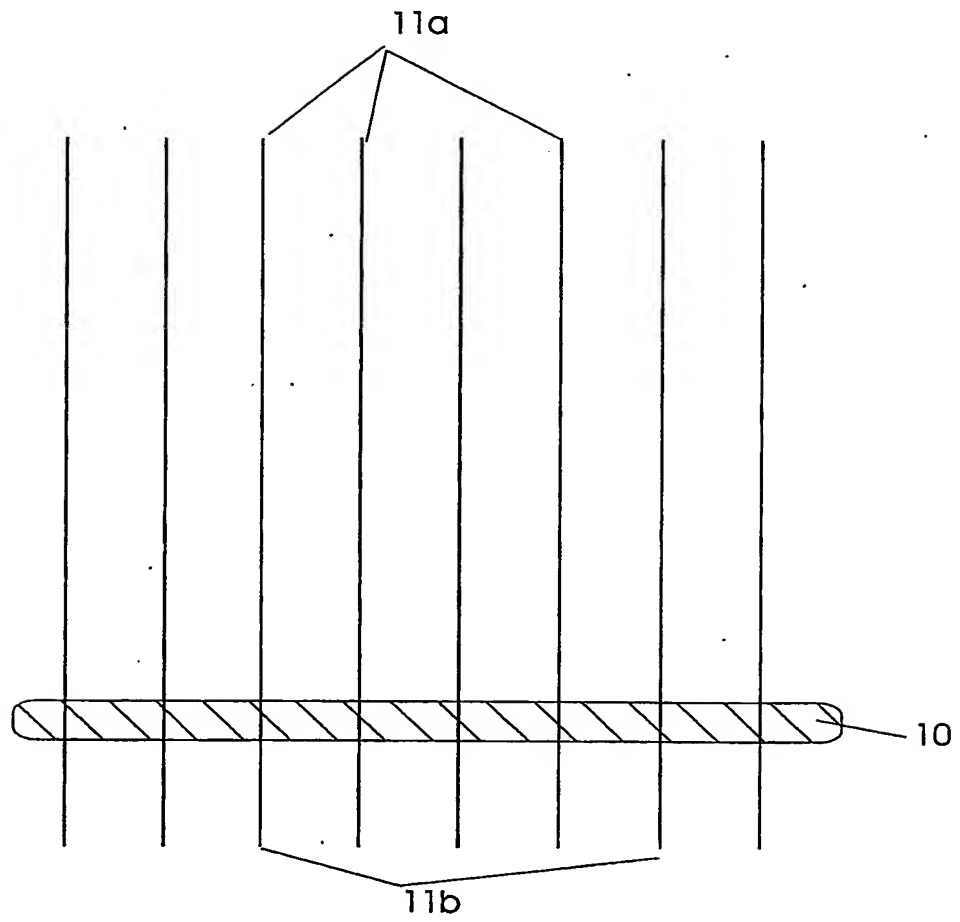


Fig. 3

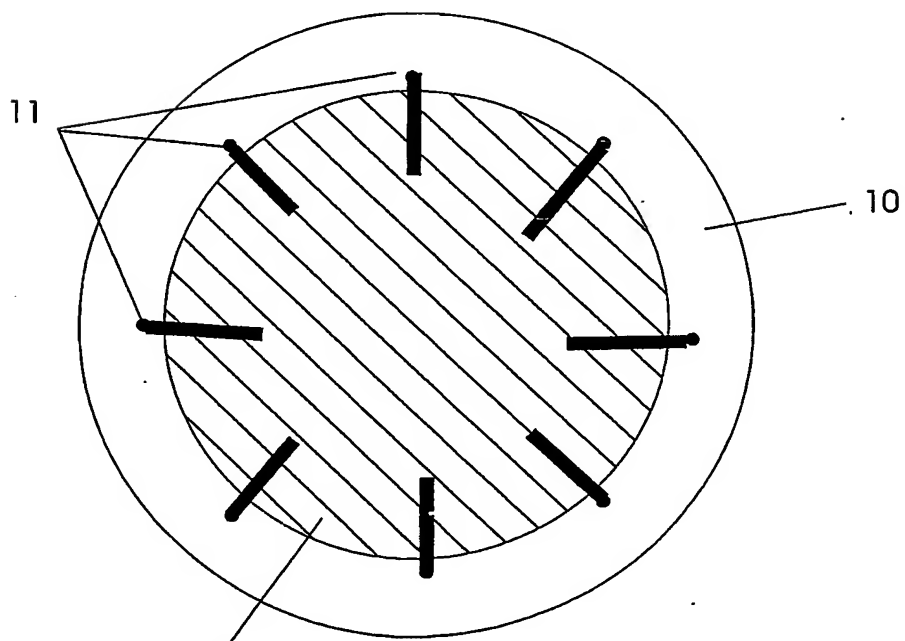


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